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THE STRUCTURE OF THE IRRADIATION PRODUCT OF THE DIHYDRO-DIELS-ALDER ADDUCT OF THEBAINE WITH DIMETHYL ACETYLENEDICARBOXYLATE

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Abstract—The structure of the title compound was determined and some of its reactions described.

It is arguable whether morphine is *the* star performer among molecular acrobats or whether it is of the same order of talent as thebaine, **1**.[1] There is, however, no doubt that to the exploits of the parent substances must be added those of their derivatives. Thebaine has an advantage over morphine in that it is a diene and may therefore react as such in Diels-Alder reactions.[2] Wheeler and Sim with their collaborators have recently reported on the structure of the photo-product **3** derived from the adduct **2** of thebaine with *p*-benzoquinone or from its diphenolic tautomer, **2a**.[3]

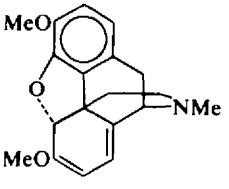
In this case the bond of C-18 moved from C-6 to C-7 whilst an electron pair involved in the double bond between C-8 and C-7 moved to join C-8 to C-6, forming a cyclopropane ring. A bicyclic di-π-methane system has rearranged to give a vinylcyclopropane.

A different type of photo-rearrangement occurs upon irradiation of the adduct **4** of thebaine with dimethyl acetylenedicarboxylate.[4] This adduct is thermally unstable due to its tendency to aromatization with concurrent cleavage of its bicyclo[2.2.2]-octadiene moiety.[5] Its dihydro derivative **6** is thermally stable[5] and since we had it in hand for a different purpose it was of interest to see whether its irradiation would afford the dihydro product **7** which corresponds to the photoproduct **5** produced from **3**, or **8** which is somewhat analogous to **3**, or alternatively, a different type of product such as **9**.

We have found that the photoproduct is in fact **7**. We have repeated the work of Kanematsu and Sasaki[4] and have found it to be correct in all respects. We add a few more details in this connection in the experimental section since we are unaware of the appearance of their full paper subsequently to the appearance of their preliminary report.[4]

In Diels-Alder adducts of thebaine with various dienophiles the low chemical shift of H-8β is interpreted in terms of shielding by the lone pair on nitrogen.[6] When the electron density in the region of the nitrogen atom is lower (owing for example to the addition of hydrochloric or trifluoroacetic acid) the line for H-8β appears at relatively higher field. If the electron density is increased, for example by the preparation of an N-oxide, again the absorption of protons in the vicinity is changed.[7] Had we been dealing with a structure corresponding to dehydro-**9** (double bond in the bridge), we would expect the presence of H-8β strongly affected by the proximity of an N-oxide and would thus expect its absorption to shift down-field.* We prepared the N-oxide by using *m*-chloroperbenzoic acid in chloroform at room temperature and noted no effect upon the chemical shift of the proton at τ 6·32, suspected on the basis of other compounds as a candidate for H-8β.† Hence we rejected this candidacy and assigned this absorption to H-5

†We shall report elsewhere significant results in which this method has proved very useful for determination of configuration in related cases (R. Rubinstein and F. Haviv, unpublished results).



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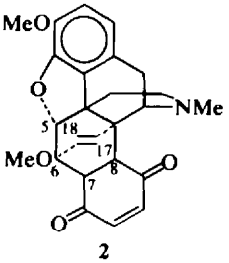

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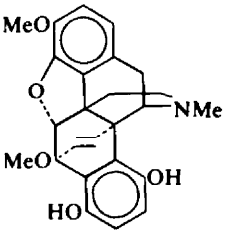

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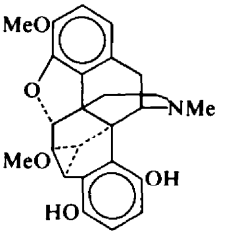

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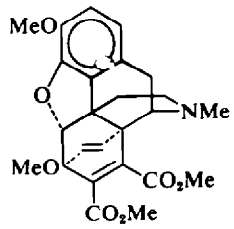

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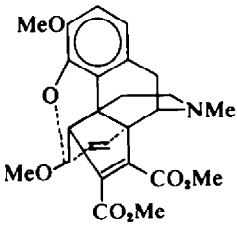

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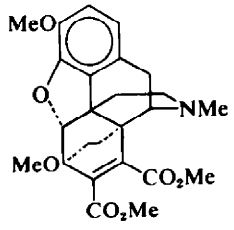

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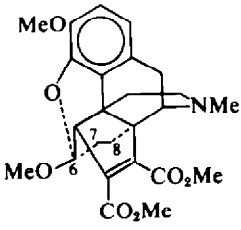

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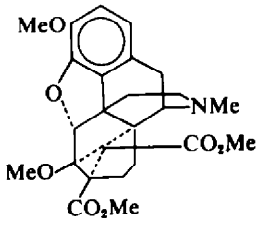

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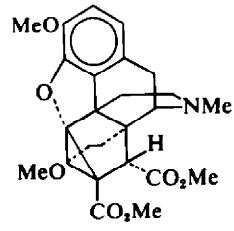


9

(suspected in any event as a candidate for reasons already published)[4,6] which would not be affected by the too distant N-oxide. Thus, more important, we have additional evidence supporting structure **5** as already proposed[4] and rejecting a structure analogous to **9**. Structures **8** and **9** are ruled out because of the interrelation accomplished between **5** and **7** through their conversions into **12** (see below).

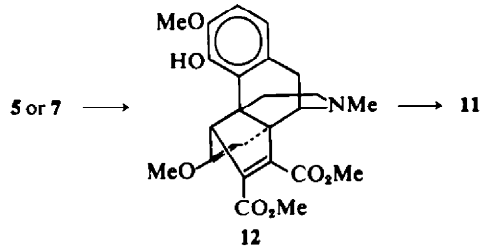
It is clear from structure **5** that neither ethylenic bond in **4** has taken part in the photoreaction (except perhaps in serving as an autosensitizer). Thus we irradiated **6** in dioxan solution with a Hanovia low pressure immersion lamp enclosed in a quartz tube (254 nm) during 6 hr. The photoproduct **7** was obtained in 44% yield. The reaction **6** → **7** does *not* occur when a Hanovia medium pressure lamp and pyrex filter (280 nm) were employed.

We obtained supporting evidence for the structure of **5**[4] inadvertently as soon as we attempted its purification by chromatography. It was sufficient to percolate a chloroform solution of **5** on a silicic acid column in order to subsequently isolate the α,β-unsaturated ketone **10**. The dihydro-compound **7** afforded **11**, i.e. dihydro-**10**.

Many attempts were made to reduce the disubstituted but evidently hindered double bond in **5** in order to prove the structure of **7**. When palladium on carbon (10%) was used in 2-ethoxyethanol as solvent two products were obtained, **10** and **11**, identical with the above.

Compound **10** is reducible to give **11** under the same reaction conditions.

Attempted diimide reduction of **5** surprisingly led to the product **12**,[4] in 33% yield. The same product **12** was obtained, even more surprisingly, when **7** was subjected to the same reaction conditions, albeit in only 14% yield. Compound **12** is an enol ether which readily affords the corresponding ketone **11** after acidic hydrolysis.



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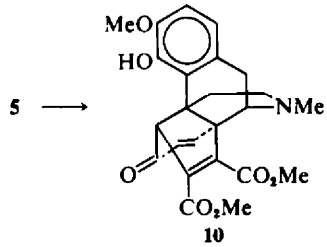
We can only attempt an explanation of the conversion of **7** into **12** by observing that the bonds oxygen to C-6 and C-7 to H-7β are disposed antiperiplanar to one another. The elimination which



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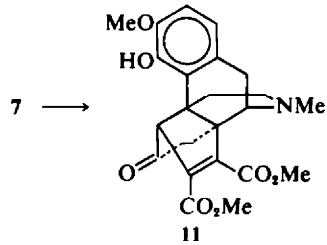

11

then occurs undoubtedly releases strain in the bicyclic system in the region of ring C compounded by substitution by the oxygen ring in this area.

We have obtained **12** from **7** by an additional, no less peculiar, route. Stirring a solution of **7** in 2-ethoxyethanol at room temperature for a week gave **12** in 53% yield. If the solvent is previously filtered through a column of basic alumina and the experiment is repeated, only **7** is recovered after a week of stirring. Evidently the conversion **7** → **12** requires a catalytic amount of (unknown) acid.

EXPERIMENTAL

UV spectra were measured on a Cary 15 and Bausch and Lomb Spectronic 505 spectrophotometers. IR spectra were measured on a Perkin-Elmer model 237 grating spectrophotometer. 60 MHz spectra were measured on a Varian T-60 spectrophotometer. Mass spectra (reported *m/e* > % of base peak) were measured in an Atlas CH 4 instrument using the heated inlet system at 200°. The electron energy was maintained at 70 eV and the ionization current at 20 μA. All m.ps are uncorrected.

For those compounds already reported in full or in part we record only those details which have not appeared.

7,8-Bis-(*Methoxycarbonyl*)-6,14-endo-*ethenocodeine methyl ether*, **4**.* Prepared according to Rapoport and Sheldrick[5] in 72% yield, m.p. 138–140° (Lit.[5] m.p. 140–142°); NMR ($CDCl_3$): τ 3·40 (ABq, J = 8 Hz, H-1, H-2); 3·78 (dxd, $J_{18,5}$ = 1·5 Hz, $J_{18,17}$ = 8 Hz, H-18); 4·46 (d, $J_{17,18}$ = 8 Hz, H-17); 5·28 (d, $J_{5,18}$ = 1·5 Hz, H-5); 6·12 (d, $J_{9\alpha,10\alpha}$ = 6 Hz, H-9α); 6·19 (s, 3 C_3—$OC\underline{H}_3$); 6·23 (s, 3 $CO_2C\underline{H}_3$); 6·26 (s, 3 $CO_2C\underline{H}_3$); 6·43 (s, 3 C_6—$OC\underline{H}_3$); 6·75 (d, $J_{10\beta,10\alpha}$ = −18·5 Hz, H-10β); 7·70–7·25 (m, H-10α, 2H-16); 7·70 (s, 3 $NC\underline{H}_3$); 8·30–8·10 (m, 2H-15); M.S. (*m/e* > 5%): 455(7), 454(36), 453(100), 452(21), 439(17), 438(63), 423(6), 422(20), 407(6), 406(21), 397(7), 394(14), 392(9), 346(7), 317(8), 236(6), 230(16), 221(7), 216(7), 189(7), 188(25), 175(7), 173(5), 115(6).

Photoproduct **5**

(a) A solution of **4** (0·45 g) in dry dioxan (75 ml) was irradiated during 4 hr under N_2, using a Hanovia low pressure (8 watt) Hg lamp shining through a quartz tube. The solvent was removed. Trituration with diisopropyl ether afforded an amorphous ppt (0·40 g; 88%), m.p. 168–174°. The cream-colored analytical sample had m.p. 180·5° (CH_2Cl_2-pentane). Lit.[4] m.p. 184°. (Found: C, 66·34; H, 5·68; N, 2·96; M.W. 453. Calc. for $C_{25}H_{27}NO_7$: C, 66·21; H, 6·00; N, 3·09%; M.W. 453·47); IR ($CHCl_3$): 1713, 1619, 1603 cm^{-1}; UV (MeOH): nm (ε) of crystallized sample: 221(22400), 240sh(12800), 293sh(5870); of amorphous compound: 239(14100), 280(4850); NMR ($CDCl_3$): τ 3·36 (s, H-1, H-2); 3·74 (d, $J_{8,7}$ = 9·8 Hz, H-8); 5·02 (dxd, $J_{7,5}$ = 2·5 Hz, $J_{7,8}$ = 9·8 Hz, H-7); 6·16, 6·19 (two s, 3 C_3—$OC\underline{H}_3$ and 3 $CO_2C\underline{H}_3$); 6·21 (s, 3 $CO_2C\underline{H}_3$); 6·32 (d, $J_{5,7}$ = 2·5 Hz, H-5); 6·39 (s, 3 C_6—OCH_3 6·90–6·40 (m, H-9α, H-10β); 7·80–7·10 (m, H-10α, 2H-16); 7·70 (s, 3 $NC\underline{H}_3$); 8·70–7·80 (m, 2H-15); M.S. (*m/e* > 5%): 455(5), 454(27), 453(100), 452(5), 438(17), 423(6), 422(19), 406(6), 395(6), 394(20), 384(5), 255(6), 230(9), 229(40), 228(33), 210(5), 204(10), 200(7), 190(6), 186(8).

(b) It is possible to obtain **5** in 76% yield using similar conditions as under (a) but replacing the lamp by a medium pressure (450 watt) Hg lamp and a pyrex filter (280 nm).

Reduction of **4**. Carried out as reported,[5] yield of **6**, 83%, m.p. 197°. (Lit.[5] m.p. 160–175°); NMR ($CDCl_3$): τ 3·31 (ABq, J = 7·5 Hz, H-1, H-2); 5·46 (d, J = 1·8 Hz, H-5), 6·10 (s, 3 $CO_2C\underline{H}_3$); 6·17 (s, 3 C_3—$OC\underline{H}_3$); 6·25 (s, 3 $CO_2C\underline{H}_3$); 6·46 (s, 3 C_6—$OC\underline{H}_3$); 6·52 (d, J = 5·5 Hz, H-9α); 6·86 (d, $J_{10\beta,10\alpha}$ = −18 Hz, H-10β); 7·40–7·75 (m, 2H-16, H-10α); 7·78 (s, 3$NC\underline{H}_3$); 7·85–9·30 (m, 6H, at positions 15, 17, 18); M.S. (*m/e* > 5%): 457(9), 456(30), 455(100), 440(30), 425(10), 424(32), 423(23), 397(9), 396(31), 365(10), 364(11), 338(7), 337(24), 268(10), 249(9), 248(48), 234(8), 220(10), 216(9), 189(9), 188(8), 176(7), 175(29).

N-*oxide of* **5**. *m*-Chloroperbenzoic acid (172 mg) was added to a soln of **5** (453 mg) in chloroform (8 ml) and the soln was stirred for 1 hr. After the usual workup and trituration in ether the N-oxide was obtained as an amorphous colorless solid (275 mg; 66% based on converted **5**), m.p. 142°. Starting material **5** (48 mg) was recovered from the ether mother liquor. (Found: N, 3·04; M.W. 469. $C_{25}H_{27}NO_8$ requires N, 2·98%; M.W. 469·47); IR ($CHCl_3$): 3660, 1723, 1708, 1630–1610 cm^{-1}; NMR ($CDCl_3$): τ 3·29 (s, H-1, H-2); 3·58 (d, $J_{8,7}$ = 9·8 Hz, H-8); 5·00 (dxd, $J_{7,8}$ = 9·8 Hz, $J_{7,5}$ = 2·5 Hz, H-7); 6·08–5·57 (m, H-9α, H-16); 6·10, 6·12, 6·22, 6·38 (4s, 6 $CO_2C\underline{H}_3$, 6 $OC\underline{H}_3$); 6·32 (d, $J_{5,7}$ = 2·5 Hz, H-5); 6·63 (s, 3 $NC\underline{H}_3$); 7·50–6·70 (m, H-16, 2H-10, 2H-15). Irradiation at 6·32 collapsed the line at 5·00 to a doublet; M.S. (*m/e* > 10%): 470(28), 469(100), 454(20), 453(13), 438(18), 410(20), 383(8), 382(32), 378(8), 310(12), 229(18), 228(12).

Photoproduct **7**

A soln of **6** (0·46 g) in dry dioxan (75 ml) was irradiated under N_2 for 6 hr using a low pressure mercury lamp (8 watt) enclosed in a quartz tube. Removal of solvent and trituration with diisopropyl ether gave a colorless solid **7** (0·20 g; 44%), m.p. 148–150°. The analytical sample had m.p. 160–161° (CH_2Cl_2-pentane). (Found: C, 65·88; H, 6·83; N, 3·30; M.W. 455. $C_{25}H_{29}NO_7$ requires: C, 65·92; H, 6·42; N, 3·08%; M.W. 455·48); IR ($CHCl_3$): 1712, 1610 cm^{-1}; UV (MeOH): nm (ε) 219(24250), 238sh (12730), 283sh (2950); NMR ($CDCl_3$): τ 3·31 (s, H-2, H-1); 6·15, 6·19 (2s, 6 $CO_2C\underline{H}_3$, 3 C_3—$OC\underline{H}_3$); 6·26 (s, H-5); 6·49 (s, 3 C_6—$OC\underline{H}_3$); 6·68–7·20 (m, H-9α, H-10β); 7·25–7·67 (m, H-10α, 2H-16); 7·72 (s, 3 N—$C\underline{H}_3$); 7·85–9·18 (m, 6H at positions 7, 8, 15); M.S. (*m/e* > 10%): 456(37), 455(100), 441(15), 440(53), 425(12), 424(47), 423(40), 396(28), 395(15), 392(12), 365(15), 364(14), 338(12), 337(43), 248(20), 175(12), 87(10).

N-*oxide of* **7**. Prepared as described for N-oxide of **5** (above), m.p. 138° (250 mg; 55%). (Found: N, 3·07; M.W. 471. $C_{25}H_{29}NO_8$ requires: N, 2·97%; M.W. 471·48); IR ($CHCl_3$): 3670, 1710, 1603 cm^{-1}; NMR ($CDCl_3$): τ 3·23 (s, H-1, H-2); 6·10–5·35 (m, H-9α, H-15); 6·14, 6·18, 6·20, 6·50 (4s, 6 $CO_2C\underline{H}_3$, 6 $OC\underline{H}_3$); 6·30 (s, H-5); 6·63 (s, 3 $NC\underline{H}_3$); 7·50–6·79 (m, 2H-10, 2H-15, 2H-16); M.S. (*m/e* > 10%): 472(25), 471(87), 456(35), 455(83), 454(13), 441(16), 440(55), 424(31), 423(17), 413(27), 412(100), 396(20), 384(10), 380(15), 337(18), 228(12).

α,β-*Unsaturated ketone* **10**. A soln of **5** (0·9 g) in chloroform (5 ml) was added to a suspension of silica gel (Merck kieselgel PF_{254}) in chloroform (70 ml). The whole was shaken for 4 hr at room temp. After removal and washing of the silica gel the solvent was removed. The ketone **10** was obtained as yellow crystals (0·45 g; 52%), m.p. 255°. The analytical sample had m.p. 256·5° (CH_2Cl_2-

*We use the nomenclature of Bentley *et al.*[8]

diisopropyl ether). Lit.[4] m.p. 270–272° (dec). (Found: C, 65·30; H, 5·58; N, 3·02; M.W. 439. Calc. for $C_{24}H_{25}NO_7$: C, 65·59; H, 5·73; N, 3·19%; M.W. 439·45); IR ($CHCl_3$): 3530 (phenolic OH), 1715 (conj. ester), 1685 (conj. ketone), 1625 cm^{-1} (C=C); UV (MeOH): nm (ε) 243-(5640), 279sh (2870); NMR ($CDCl_3$): τ 3·03 (d, J = 10 Hz, H-8); 3·56 (s, H-2, H-1); 4·30 (s, phenolic OH. exchanged in D_2O); 5·60 (dxd, $J_{7,5}$ = 2 Hz, $J_{7,8}$ = 10 Hz, H-7); 5·52 (d, $J_{5,7}$ = 2 Hz, H-5); 6·17 (s, 3 C_3—OCH_3); 6·21 (s, 6 CO_2CH_3); 6·51 (d, $J_{9\alpha,10\alpha}$ = 5·5 Hz, H-9α); 6·89 (d, $J_{9\alpha,10\alpha}$ = 5·5 Hz, H-9α); 6·89 (d, $J_{10\beta,10\alpha}$ = −18 Hz, H-10β); 7·37 (dxd, $J_{10\alpha,9\beta}$ = 5·5 Hz, $J_{10\alpha,10\beta}$ = −18 Hz, H-10α); 7·87–7·39 (m, 2H-16): 7·70 (s, 3 NCH_3; 8·58–7·87 (m, 2H-15); M.S. (*m/e* > 10%): 439(100), 408(13), 383(11), 382(40), 380(16), 352(18), 323(16), 322(25), 262(21), 250(34), 249(29), 243(29), 242(40), 230(10), 229(17), 228(58), 218(22), 204(10), 196(18), 58(15), 42(22).

The *hydrochloride of* **10** was obtained from **5** (0·45 g) in acetone (10 ml) upon adding conc HCl (10 drops). After 5 min the salt precipitated as yellow needles (0·25 g; 53%), m.p. 240° (dec). (Found: N, 2·70; M.W. —HCl, 439. $C_{24}H_{26}NO_7$. HCl requires: N, 2·94%, M.W. 475·91). IR ($CHCl_3$): 3525, 3380(br), 2700–1900(br), 1738, 1706, 1630 cm^{-1}. The mass spectrum was practically superimposable upon that of **10**; NMR (DMSO-d_6): τ −0·85 (br s, ^+NH. exchanged by D_2O); 1·04 (br s, OH. exchanged by D_2O); 2·66 (d, $J_{8,7}$ = 9 Hz, H-8); 3·20 (ABq, J = 8 Hz, H-1, H-2); 4·64 (dxd, $J_{7,5}$ = 1·8 Hz, $J_{7,8}$ = 9 Hz, H-7); 5·47 (m, H-9α, H-16); 5·72 (d, $J_{5,7}$ = 1·8 Hz, H-5); 6·18, 6·23 (2s, 6 CO_2CH_3, 3 OCH_3); 6·40–7·00 (m, H-16, H-10β, H-10α) 7·14 (s, 3 NCH_3); 7·20–8·20 (m, 2H-15).

Reduction of **5**. A mixture of **5** (0·23 g), Pd-C (10%; 12 mg) and 2-ethoxyethanol (5 ml) was shaken with hydrogen at 50 psi for 3 hr at room temp. The catalyst and solvent were removed. The residue was taken up in benzene and the soln was chromatographed on basic alumina (grade V; 20 g). A mixture of **10** and **11** was obtained (0·17 g). It was not possible to effect quantitative separation of the two. The mixture was therefore dissolved (or pure **10** was dissolved) in 2-ethoxyethanol (10 ml) and ethanol (5 ml) and the soln was shaken with Pd-C (10%; 10 mg) and H_2 at 49 psi for 24 hr. Compound **11** was obtained still contaminated with a small amount of **10**. To a certain extent it was possible to separate **10** from **11**. A second chromatography as above afforded **10**, m.p. 241–242° (chloroform-ether). Compound **11** was eluted later, m.p. 210° (chloroform-ether).

Preparation of pure **11**

(a) To a soln of **7** (0·22 g) in dry benzene (25 ml) was added a small amount of *p*-toluenesulfonic acid and the mixture was allowed to stand at room temp for 10 min. After washing with $NaHCO_3$ aq, water and drying (Na_2SO_4), the solvant was removed. The ketone **11** (0·21 g; 98·5%) had m.p. 209° (chloroform-ether). (Found: C, 65·63; H, 6·26; N, 3·09; M.W. 441. $C_{24}H_{27}NO_7$ requires: C, 65·29; H, 6·16; N, 3·17%; M.W. 441·46); IR ($CHCl_3$): 3535 (phenolic OH), 1725 (CO), 1630 cm^{-1} (C=C); UV (MeOH): nm (ε) 235sh (7920), 283 (3240); NMR ($CDCl_3$): τ 3·26 (s, H-1, H-2); 4·21 (s, phenolic OH, exchanged in D_2O); 5·88 (s, H-5); 7·12, 7·15, 7·20 (3s, 6 CO_2CH_3, 3 C_3—OCH_3); 6·40–7·40 (m, H-9α, H-10β, 2H-7); 7·40–7·65 (m, H-10β); 7·69 (s, 3 NCH_3); 7·80–9·00 (m, 2H-8, 2H-15, 2H-16). M.S. (*m/e* > 10%): 442(23), 441(100), 410(11), 382(30), 354(25), 328(10 297(15), 296(23), 204(25), 58(21), 44(12), 42(17).

(b) *From* **12**. 2N HCl (0·6 ml) was added to **12** (30 mg; see below). After 20 min at room temp the soln was diluted with water and NH_4OH aq was added. After extraction with CH_2Cl_2 drying (Na_2SO_4) and removal of solvent, pure **11** (18 mg; 62%) was obtained, m.p. 209–210° (ether), identical with that prepared by procedure (a) above.

Preparation of **12**

(a) A soln of **5** (1·36 g) in dry pyridine (75 ml) was treated with dipotassium azodicarboxylate (12 g). To the yellow suspension was added with stirring during 1 hr glacial AcOH (3 ml) in dry pyridine (15 ml). Stirring was continued for 40 hr. A similar addition of AcOH (3 ml) in pyridine (15 ml) was made after 16 hr. The mixture was filtered through celite and the pyridine was removed in a vacuum. The crude material was dried in a high vacuum. Its soln in benzene was chromatographed over basic alumina (grade V). The product **12** was eluted with chloroform (1): benzene (9) (0·45 g; 33%), m.p. 210–211°. The analytical sample had m.p. 215–216° (CH_2Cl_2-EtOH). Lit.[4] m.p. 231–234°. (Found: C, 65·63; H, 6·55; N, 3·08; M.W. 455. Calc. for $C_{24}H_{29}NO_7$: C, 65·92; H, 6·42; N, 3·08%; M.W. 455·48); IR ($CHCl_3$): 3534, 1713, 1662, 1626 cm^{-1}; UV (MeOH): nm (ε) 233sh (9700), 280(3380); NMR ($CDCl_3$): τ 3·29 (s, H-1, H-2); 4·33 (s, phenolic OH exchanged in D_2O); 5·94 (m, H-7), 6·13, 6·17, 6·20 (3s, 6 CO_2CH_3, 3 C_3—OCH_3) 6·57 (s, 3 C_6—OCH_3); 6·50–7·68 (m, H-9α, H-10β, H-5, 2H-8): 7·72 (s, 3 NCH_3); 7·70–9·60 (m, H-10α, 2H-15, 2H-16), M.S. (*m/e* > 10%): 455(92), 441(27), 440(100), 424(12), 396(27), 230(23).

(b) A soln of **7** (0·46 g) was treated exactly as **5** in procedure (a). Product **12** (52 mg; 14%) was isolated and about half of **7** was recovered. The colorless **12** had m.p. 211–212° and was identical to that described above.

(c) A soln of **7** (114 mg) in 2-ethoxyethanol (1·5 ml) was stirred at room temp for 144 hr. The solvent was removed and the residue was taken up in benzene and chromatographed over neutral alumina (containing 10% H_2O; 10 g). It was eluted with chloroform. The crude product **12** (60 mg; 53%) had m.p. 198° (EtOH). It had identical spectral properties to the product described above.

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